

Contemporary Advances in Physics, XVII The Scattering of Light with Change of Frequency

By KARL K. DARROW

SCATTERING of light is one of the commonest of all phenomena, which does not in the least imply that it is one of the most commonplace. Even its practical importance entitles it to high respect. We are often told that were it not for scattering, the sky would not be blue; the sun and the stars would stand out amazingly brilliant against a background black as coal. It is probable, however, that if scattering were suddenly to be suspended, the disappearance of the sky would be one of the least of our worries. Everything else would disappear, except what was self-luminous. The visible world would consist of the sun, the other stars, and flames, some electrical discharges, the filaments of incandescent lamps, and some substances glowing feebly with fluorescence or phosphorescence. Nothing else could be seen except as a silhouette, apart from objects so translucent that they could be viewed as a stereopticon slide against a flame. Happily no such calamity impends; and we may unconcernedly consider the theoretical importance of the process, which is great. As some might say, the scattering of light is one of the battlegrounds between the undulatory and the corpuscular theories. Metaphors of combat are however not appropriate; it is necessary to reconcile the theories, not to smash one or the other. Now it happens that some of the phenomena of scattering may be interpreted by the one theory, and some by the other; and some can be explained by either, which is most auspicious; for if this can some day be said of all the phenomena of light, the goal of our desires will have been attained.

Also scattering of light has just sprung into prominence as the most inviting and the most ardently invaded field of physics, because of a discovery such as, it had been supposed, could never happen again. It seemed that experimental physics had been so thoroughly developed—or, to change over to an ancient metaphor, that the field had been so thoroughly harvested and then so exhaustively gleaned—that nothing important could possibly remain to be discovered unless by measurements of great precision, or by radically new apparatus, or by applying voltages or other agencies on a scale as yet untried. Yet in the spring of 1928 a mode of scattering of visible light was discovered,

by a physicist working with a quite ordinary spectroscope, a quite ordinary source of light and some very familiar chemicals, all of which had been available to everyone for at least fifty years. The physicist who thus saw what for half a century the whole world had overlooked was C. V. Raman of Calcutta.

Within a few months it was observed that what Raman had discovered was one of the special cases of a very general principle, which had already been stated almost as clearly as one can state it even today, but had failed of due recognition, evidently for want of some conspicuous example. Other special cases had indeed already been discovered among the phenomena of X-rays, but for some reason or other all except one had failed to make the impression which they should have made. Raman's discovery brought the principle sharply into relief. I shall not state it fully at this point; but this is its practical consequence: *when light falls upon matter, the scattered rays need not all have the same frequency as the infalling.* Most of the scattered light may preserve the initial frequency unchanged as formerly it was supposed that all did; but some part of it may be modified or shifted.

The present paper is devoted to this principle almost entirely; but to give it the proper background, I must at least mention some of the other aspects of scattering. Light may be scattered by particles of any size, from atoms up to grains of dust or droplets of mist; even the reflection from larger bodies is to be considered as the resultant of light-scattering from the particles of which these are made. Scattering by granules or droplets may be analyzed by the electromagnetic theory, the substance of the particle being considered as a medium with a different index of refraction and a different coefficient of absorption from the surrounding air. This however is distinct from the case with which we have now to deal, the scattering of light by molecules or atoms—although the transition from one type to the other should be very interesting and instructive.

The effect produced by molecules or atoms—it is known as the Tyndall effect, from its earliest thorough student—is fairly conspicuous in liquids or crystalline solids, though a very small trace of dust or finely-dispersed precipitate produces a brilliant scattering which completely overwhelms it. In gases it is difficult to see, but not impossible. The blue of the sky is a specific instance which is easy to observe, because the air is so deep.

The features of the scattered light which are commonly studied—I am speaking now of the time when it was assumed that there is no change in frequency—are its intensity, its polarization, and a property which is rather vaguely known as "coherence." The intensity of the

light scattered from an incident beam, of which the wave-length is varied while the intensity is kept constant, increases very rapidly indeed with decreasing wave-length—in some cases, as the inverse fourth power of the wave-length. (This is the reason why the sky is blue; the molecules of oxygen and nitrogen are not especially tuned to blue light, but the waves from the sun are more powerfully scattered the nearer they lie to the violet end of the visible spectrum.) The scattered light is more or less polarized, even when the primary light is not polarized at all. In some cases the light deflected through 90° is perfectly plane-polarized; by the undulatory theory this signifies a very simple sort of vibrator in the atom, a vibrator which is attracted by an equal restoring-force whichever way it is displaced from its centre of vibration. In other cases the polarization is different, and other inferences about the atom-model may be drawn from it. As for the "coherence," it is a very important property—important for the theorist. If the scattering atoms contain vibrators which the infalling waves maintain in forced oscillations, and which themselves send out the scattered light, then these scattered or "secondary" wave-trains should interfere with one another. If in particular the vibrators, or let us say the atoms, form a regular lattice in space—a cubic lattice, for example—there should be destructive interference; the secondary wavetrains should completely destroy one another in all directions save that of the ongoing primary beam,¹ and there should be no perceptible scattering at all. The perceptible scattering is then a measure, to speak rather vaguely, of the *irregularity* in the arrangement of the atoms. This theory seems to be confirmed, for the light scattered without change of wave-length. Whether it is true also for the shifted light will probably soon be known.

Scattering of light with unchanged frequency is easy to explain by either wave-theory or corpuscle-theory. To those who think of light as waves and of atoms as systems of vibrators, it is a consequence of forced vibrations. The fluctuating or alternating electric field which—coupled with an alternating magnetic field—constitutes the beam of light, seizes upon an electrified portion of the atom and swings it to and fro in synchronous vibration. From this swinging electric charge, the scattered waves originate. It is evident that the forced vibrations and the scattering should be especially intense, when the frequency of the light coincides with a natural frequency of vibration of the atom, for then there is resonance. Now it is a fact that scattering is especially intense, when the infalling light agrees in frequency with any of

¹ More precisely, in all directions save those of the Laue diffraction-beams, which however for crystals and visible light do not occur.

certain spectrum lines which the atom may emit spontaneously. To those who think of light as a hail of corpuscles—"quanta"—scattering is rebounding of the quanta from atoms which they strike "elastically"; that is to say, as one elastic sphere striking another. This is easy to picture; but then we are left without any obvious explanation of the fact which was just mentioned—the fact that this sort of rebounding takes place especially often, when the quanta agree in frequency with those which the atom can naturally emit. Finally, for the single case in which the incident frequency agrees with that of a spectrum line and the scattering is very abundant, one can employ a compromise-theory; the atom is struck as by a bullet which sets it to vibrating freely with one of its own natural frequencies, as a bell which is struck by its clapper.

Scattering of light with change of frequency is certainly more complicated. The advocates of waves and oscillators must conceive that in the atom there goes on a process similar to what, in the art of electrical communication, is known as *modulation*. The frequency of the infalling light is modulated with some frequency characteristic of the atom. If the compromise-theory is valid, there are several cases in which one easily sees how this happens. Thus if a straight spring is alternately contracting and expanding with a frequency n_0 , and at the same time is revolving around an axis perpendicular to its length with a constant angular velocity $2\pi n_1$, its ends will seem to a stationary observer to be moving with a motion compounded of two frequencies— $(n_0 + n_1)$ and $(n_0 - n_1)$; and if waves are sent out, they will have these frequencies jointly.² If the "spring" is an electrical doublet lying perpendicular to a magnetic field, it revolves automatically as it vibrates, and sends forth electromagnetic waves which are discriminated by the spectroscope into two lines of these two frequencies. Such is the explanation by wave-theory of the "normal Zeeman effect"; and while the actual effect of magnetic fields upon the light emitted by the atoms which they influence is not often exactly thus, it is sufficiently nearly so to prove that this interpretation is a step on the right path. If however one wishes to maintain the uncompromising wave-theory, and suppose that the vibrators in the atoms are kept going in forced vibration by the continually-acting waves of light, then modulation does not necessarily occur—not at least with the con-

² This idea was introduced by the elder Lord Rayleigh in the course of some speculations on the emission of light by rotating atoms, and was later turned to account in explaining the fine-structure of the bands which constitute the spectra of molecules.

ventional atom-models.³ Models however can be devised which account for modulation, and perhaps they will become more popular.⁴ In one simple case related to the Compton effect, forced vibrations result in waves which do not coincide in frequency with the primary waves; this is the case of a free electron, which the magnetic force in the light-stream pushes more and more rapidly forward as the electric force makes it swing more and more rapidly crosswise; and as the electron gains speed, the frequency of the waves which it sends to a stationary observer steadily sinks.

To the thoroughgoing advocate of the corpuscle-theory, however, the problem of the scattered light of shifted frequency seems simple; or, at all events, the first step in explaining it seems obvious. Frequency of light, when multiplied by the universal constant h , is the measure of the energy of the corpuscles of the light. Change of frequency therefore means transfer of energy. If a quantum of frequency n_0 flies onto an atom and a quantum of frequency n_1 flies away, energy in the amount $h(n_0 - n_1)$ stays behind with the atom. If n_1 is greater than n_0 , as sometimes happens, the departing quantum takes with it some energy which belonged to the atom as well as all that was brought by the oncoming quantum. As yet there is no picture of the process by which the energy is passed between the matter and the light. But we are not supposed to ask the quantum-theory for such pictures. Perhaps one reason why it seems so much stronger than the wave-theory is, that of the latter we have expected so much more.

However, visualizable or not, the corpuscle-theory implies that if the scattered light differs in frequency from the infalling light, individual molecules or atoms are receiving or giving energy in quantities equal to the frequency-difference multiplied by h . Not any and every amount of energy may be annexed or ceded by a molecule or an atom—only certain sharply definite, distinct and separate amounts, equal to the energy-differences between the state in which the particle happens initially to be, and one or another of its various other “permitted” stationary states. There are exceptions to the rule, as I will state immediately; but in experiments performed with visible light they are not apparent. Correspondingly the frequency-shifts of the scattered light are limited to certain distinct and separate values;

³ Thus an electron which is subject at once to a quasi-elastic restoring-force, a sinusoidal electric field, and a constant magnetic field perpendicular to the electric field, describes a fixed orbit with a single frequency equal to that of the electric force, and there is no modulation. Mistakes in this respect have been made by various people who theorized about the Wood-Ellett effect.

⁴ Such models have been devised by Hartley and by Kennard.

the spectrum of the scattered light due to a single primary spectrum line consists of that line accompanied by a number of others, separate from it and from one another. Intermediate frequencies do not occur, for they would correspond to transfers of energy in quantities which the atoms are not able to offer or accept. The shifted lines which do occur, the "Raman lines," reveal the energy-values of the stationary states of the scattering particles.

We consider next the exceptions to the rule—the cases in which a scattering particle may accept or surrender any quantity of energy whatever within an appreciable continuous range, instead of merely certain separate discrete amounts. This may be possible if the energy conceded by the quantum is employed in altering the speed of the particle, or in breaking the particle into pieces and imparting speed to these—if it becomes kinetic energy of translatory motion of the molecule or atom, or of the fragments thereof. Translatory motion is non-quantized, which is a way of saying that it is not under the dominion of quantum-conditions which allow to it some values and deny it others. Any amount of kinetic energy of translation is permitted to a molecule or an atom, so far as we know. This suggests that any amount of energy may be transferred when such a particle meets a corpuscle of light, provided that so long as the energy is held by the molecule or the atom it is held in this form. But there is another limitation to be remembered—that imposed by Newton's principle of the conservation of momentum. If a swiftly-moving corpuscle of relatively small mass m strikes a slowly-moving body of much larger mass M , the latter cannot gain much speed in the encounter; for it cannot acquire speed without acquiring momentum, and if it were to accept for that purpose more than a very small fraction of the energy of m , it would have to take more momentum than all that m possesses.

Now relatively to an atom, a corpuscle of light is a body of very small mass and very swift flight indeed; and a quantum of frequency n cannot transfer to an atom of mass M , for use as kinetic energy of translation, more than the fraction $2hn/MC^2$ of its own initial energy—more than the quantity $2h^2n^2/MC^2$ altogether.⁵ For a quantum belonging to the visible spectrum the fraction $2hn/MC^2$ is of the order of 10^{-8} even for an impact with the lightest of all atoms. The utmost possible shift in frequency of the scattered light would bear only this proportion to the primary frequency, and would be indistinguishable. But the higher the frequency of the quantum, and the lower the mass of the

⁵ The formula is approximate, but the approximation is very close in all practical cases. For the derivation of this and the accurate formula, see A. H. Compton, *Bull. Nat. Res. Council*, 20 (1922) or my *Introduction to Contemporary Physics*, pp. 148–149.

scattering particle, the greater this maximum possible transfer of energy and this maximum possible frequency-shift become; and for a collision between an X-ray quantum and a free electron, it attains the order 10^{-2} of the primary frequency, and is very appreciable. In fact, the frequency-shift occurring when X-ray quanta transfer energy to free electrons and these employ it as kinetic energy was the first of all to be observed. It is simply the Compton effect. It was noticed first towards 1904 and was described as "softening of the scattered X-rays," and in 1922 was for the first time properly measured and properly interpreted by Arthur Compton. The scattered rays include every frequency from that of the primary rays, n_0 let us call it, downward to the lower limit $(1 - 2hn/MC^2)n_0$, as they should.⁶

If the primary quantum breaks the particle which it strikes into two or more fragments—as for instance when an atom is ionized or a molecule dissociated—the requirement of conservation of momentum no longer limits the amount of energy which it may pass to these. It must give at least enough energy to ionize or to dissociate the particle; beyond this, so far as we know *a priori*, any extent of transfer is permitted. Hence we should expect to observe in the spectrum of the scattered light a continuous band, commencing at the frequency which is less than that of the primary light by the quotient of h into the ionizing-potential or the dissociation-potential, and extending towards lower frequencies indefinitely far. More precisely, we should expect to observe as many of these bands as there are modes of dissociation or modes of ionization feasible by light.

No one, so far as I know, has yet observed any bands corresponding to dissociation of molecules or to the detachment of loosely-bound electrons by visible or ultra-violet light. In the X-ray region, however, it is different. In the spectra of scattered X-ray bands answering to this description, and suggesting that X-ray quanta have extracted deep-lying tightly-bound electrons from atoms and have conferred kinetic energy upon them, have in fact been reported. Several such spectra were depicted in 1923 and 1924 by G. L. Clark and W. Duane.

If it should turn out in any special case that quanta could extract electrons from atoms, but could not confer extra kinetic energy of translatory motion on them—a restriction which there is no evident

⁶ This is disguised by the fact that the rays scattered in any one direction (relatively to the primary beam) are of a single frequency. If we observed simultaneously rays scattered in all directions, we should see a continuous band of light extending between n_0 and the stated lower limit. This condition was approached, though not purposely, in some of the earlier researches on the Compton effect.

The shift which should occur if quanta of the visible spectrum are scattered by free electrons is very small, but sufficiently large to be appreciable; however, this type of scattering does not seem to occur to a perceptible extent, for it has been sought in vain (P. A. Ross).

reason to foresee—then the aforesaid bands would be reduced to lines, shifted from the primary line through frequency-intervals equal to the ionizing-potentials divided by h . Such lines were observed in the early spring of 1928 by B. Davis and D. P. Mitchell, in the spectrum of X-rays scattered by graphite.

There is one more way in which corpuscles of light can dispose of part of their energy—in setting into vibration atoms which are built into the structure of crystal lattices. Many crystals behave as if they contained oscillators having natural frequencies of the order 10^{12} – 10^{14} , and able to emit light of the corresponding wavelengths, which are in the infra-red region of the spectrum. Some of the quanta which strike such a crystal lose energy in being scattered, and the energy which they lose is equal to h times one or another of these oscillation-frequencies. This effect was discovered independently in the late winter or early spring of 1928 by G. Landsberg and L. Mandelstam, and by C. V. Raman and K. S. Krishnan.

Presently I will quote in more detail the data which establish all these facts; but first it is urgent to point out that there is another phenomenon in nature, a phenomenon long known and well known, with which the scattering of light with altered frequency can readily be confused; indeed it is often difficult, and I suspect that it may sometimes be impossible, to tell whether in an actual case we have the one or the other before us. I refer, of course, to fluorescence. The description of fluorescence, indeed, reads exactly like the description of scattering of light with change of frequency. Light of one frequency falls upon a substance, and light of another frequency emerges from it. How then shall we discriminate between the two?

According to the ordinary conception of fluorescence—a conception which has attained to the rank of a definition—the molecule or the atom absorbs a quantum of the incident light, and is put thereby into an excited state; and after a longer or a shorter time, it passes spontaneously into a state different both from the excited and from its original state, and emits a quantum which is not of the same frequency as the one which it absorbed. (I am considering fluorescence of gases or of dilute solutions, where one can suppose that the quanta are absorbed or emitted by individual molecules; more complex cases are too complex, for the time being.) Let the original state be symbolized by N , and the final state by A , and the temporary state by B ; denote by $E_{AN} = hn_{AN}$ the energy-difference between A and N , positive if the energy in state A is the greater; use the letters n_{BN} and n_{BA} correspondingly, and denote by n_0 the primary frequency. Then there will be no fluorescence at all unless $n_0 = n_{BN}$; unless, that is to

say, the primary quanta have exactly the right energy to transfer a molecule from its original state to some other (excited) state. Suppose however that this condition is fulfilled; then the quantum of fluorescence-light is emitted when the molecule passes from state B to state A , and therefore has the frequency n_{BA} . But because of the energy-relations, we have

$$n_{BA} = n_{BN} - n_{AN} = n_0 - n_{AN},$$

which means that the quantum of fluorescence-light has exactly the same energy as a quantum of the primary light would retain, if it had been scattered from the molecule after communicating to this latter the energy requisite to transfer it from its original state N to the state A . The fluorescence-light is shifted in frequency from the primary line by exactly the same interval as the Raman line corresponding to the transfer of the molecule from N to A .

It follows then that one can never decide by measurement of wavelength whether a line in the scattered light is due to fluorescence or to scattering with change of frequency.⁷ This is inevitable; for in either case the molecule involved in the process starts from the same initial and ends in the same final state, and the frequency of the departing quantum depends on nothing but the difference between these two. The only question at issue is, whether the molecule has gone from the initial to the final state directly, or *via* the temporary state B .

One way of solving the question seems obvious: to vary the frequency of the light with which the molecules are irradiated, and notice whether the shifted line which is under observation—a line is identified by the amount of its shift, not by its actual frequency, so that a given line travels along the spectrum *pari passu* with the primary light—makes its appearance when and only when the quantum-energy hn_0 of the primary beam coincides with the energy-difference between the initial state of the molecule and any one of its other states. In other words: does the shifted line appear only when the primary quanta can be absorbed by the molecules—when the infalling light coincides with a line of the absorption-spectrum of the substance? or does it appear always? If the latter is the case, it is the Raman effect which we have before us, at least when the wave-length of the infalling light is such that its quanta are not absorbed.

If however the shifted line is most intense when the primary fre-

⁷ This may be too strongly stated; one might observe a fluorescence-line emitted—to use the foregoing symbols—by reason of the transition from A to N (not that from B to A) which could not be a Raman line correlated with a transfer of the molecule out of the state N . On the other hand it could be a Raman line associated with a transfer of the molecule out of state A , so that one would have to assess the relative likelihoods of the states A and N among the molecules.

quency coincides with a frequency in the spectrum of the scattering substance, it does not necessarily follow that we are dealing with a case of fluorescence. Scattering without change of frequency is very much intensified, when such coincidence is brought about. Experience teaches this, and the wave-theory also; for a vibrator scatters waves most powerfully, when they and it are in resonance together. Scattering with change of frequency may follow the same rule. The proof of fluorescence, then, turns finally on this: can it be shown that there is an interval of time between the moment when the primary quantum impinges on the molecule, and the moment when the secondary quantum leaves it?

Often with solid substances one can actually see that the secondary rays continue to emerge for an appreciable time after the primary rays are discontinued; but with gases no such great delay has so far been observed.⁸ However, there are sometimes indications that between the arrival of the primary quantum and the departure of the secondary quantum, there is an interval of time during which something can happen to the molecule or atom—something which changes the nature of the departing quantum, and may even prevent it from ever being born. Pure rarefied gaseous mercury and sodium and iodine, to take three instances, emit light vividly when they are illuminated; but if they are made very dense, the intensity of the emitted light is much reduced, or its spectrum is entirely changed, or both of these things happen; so also when they are mixed with gases such as hydrogen or argon.

Such results, it is clear, are difficult or impossible to explain if the emitted light consists of primary quanta which have rebounded *instantaneously* from collisions with (say) mercury atoms; for such collisions would be more numerous when the gas became denser, and not much less numerous when the gas was diluted with argon; and the rebounding quanta would vary proportionately in number, while the frequency-shifts which they display would not be changed (unless one were to hit two or more atoms in succession). However, if the mercury atoms absorb the primary quanta, and hold on to their energy for a while, and subsequently by some independent process release it, all these effects are quite easy to interpret. The atom which has accepted the energy of a quantum, and has not yet decided to disgorge it in the form of a secondary quantum, may meet another atom and unload the energy in part or altogether. It is certain that this can happen; for when mercury vapor is mixed for instance with thallium

⁸ Methods whereby it might be possible to measure the time-interval have been suggested by Ruark.

vapor and the mixture is bombarded with quanta which mercury atoms can absorb and thallium atoms cannot, we nevertheless presently find the thallium atoms possessed of some of the energy which was sent in. Collisions of atoms occur more frequently, the denser and the warmer the gas or the mixture of gases becomes; the opportunities for diversion of energy, which otherwise would be re-radiated as fluorescent light, become correspondingly more numerous. When therefore the light emitted by an illuminated gas changes its spectrum or fades away as the gas is densified or contaminated, the probabilities are that it is true fluorescence-light.⁹ The influence of a magnetic field upon the character of the emitted light may also furnish evidence.

One sees therefore that the distinction between scattering and fluorescence is by no means immediate. Even the case which seems most explicit of all—where the primary light agrees with one of the spectrum-frequencies of the atom and the secondary light is unshifted, as when rarefied sodium vapor is illuminated by one of the *D*-lines and re-radiates it—is not exempt from doubt. Very likely part of the re-radiated rays is fluorescence-light and part consists of scattered quanta. It is obvious why Raman thought at first that he was observing fluorescence. Others very likely had already noticed the Raman effect, and classified it merely as another instance of the already well-known phenomenon.

I will now relate some of the details of the recent experiments which have suggested that light may actually be scattered with change of frequency.

THE RAMAN EFFECT

The scattering of visible¹⁰ light with change of frequency was first discovered by a man who was working with molecular liquids. It is interesting and instructive to consider why the effect, so obvious under these circumstances, had eluded the numerous and notable physicists who had studied—exhaustively, it was thought,—the influences of light on gases and of gases on light.

In the first place, a liquid contains many more molecules per unit volume than a gas, and therefore offers many more opportunities for collisions of quanta with molecules. This is essential, for collisions which result in excitation of the molecule and in scattering of the quan-

⁹ I suspect that Saha, in concluding that the resonance-spectra of vapors discovered by Wood are actually examples of scattering with change of frequency, did not take sufficient account of some of these phenomena. Consider for instance those observed by Wood and Loomis (*Jour. Franklin Inst.*, 205, pp. 489-495).

¹⁰ I will reserve the name "Raman Effect" for the scattering with shift-of-frequency of light of the visible and adjacent ranges of the spectrum, as in the X-ray region the effect was earlier discovered.

tum with altered frequency are evidently relatively rare; otherwise they could not have escaped the notice of those who have studied gases.¹¹ Even scattering without change of frequency is unusual, unless the primary light coincides exactly with a spectrum-line of the molecule; the blue of the sky is conspicuous only because the air is so thick; in the laboratory, light scattered with unshifted wave-length by a gas can be seen only if the gas is dense, the primary light blindingly brilliant, and the eye thoroughly rested.

But if it had occurred to any physicist to seek for the effect with (say) mercury atoms, by crowding the atoms together into the liquid form, he would certainly have rejected the idea the moment after it flashed across his mind; indeed it would probably never have flashed; for as

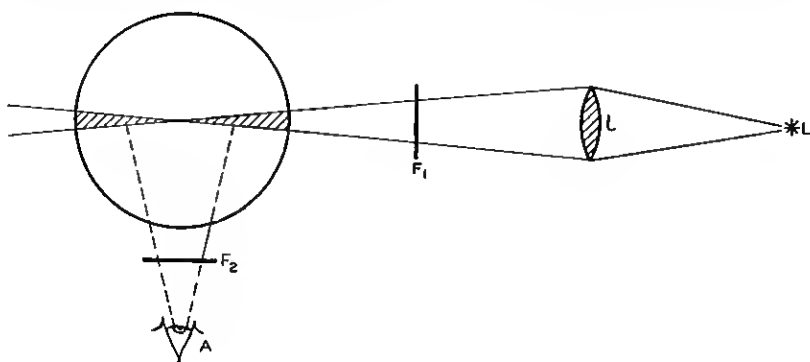


Fig. 1—Sketch of scheme for observing fluorescence and scattering.
(After Pringsheim.)

soon as atoms are forced into such close proximity, their excited states, or those at least with which we are now concerned, simply disappear. The *free* mercury atom, for instance, has a "4.9-volt" excited state—that is to say, a stationary state into which it will pass over, if being initially in its normal state it receives an acceptable offer of 4.9 equivalent volts of energy. Were we to bombard mercury vapor with 6-volt quanta—i.e. with corpuscles of light, each possessing 6 equivalent volts of energy—we might expect some of these to transfer 4.9 equivalent volts to atoms which they strike, and rebound as 1.1-volt quanta. But there is no reason to expect anything of the sort with *liquid* mercury; there is no reason to suppose that the atoms are avid to grasp this particular amount of energy, and plenty of reason to suppose that they are not. The same holds for every other excited state of a free atom, of which the energy-excess over the normal state is smaller

¹¹ Also one would expect to find, in the light scattered from liquids, quanta which have suffered two or more collisions; such have not yet been reported, so far as I know.

than the energy at the disposal of corpuscles of visible or ultra-violet light. Modern atomic theory makes this vanishing of the excited states seem very plausible; for the said excited states correspond to particular arrangements of the electrons at the surface of the atom, which are completely disorganized when atoms are crowded close together. But, apart from theory, it is an experimental fact.

One can therefore scarcely hope to find scattered light with a spectrum composed of discrete separate lines, unless one can find atoms or complexes of atoms of which the low-energy excited states remain discrete, separate and accessible when the substance is liquefied or solidified. With atoms, as I have said, this appears to be impossible. The high-energy excited states, in which one or another of the deep-lying electrons is absent from the atomic system, are indeed the same whether the atoms are free or are crowded together into a solid or a liquid; but corpuscles of light of the visible or the ultra-violet spectrum have not energy enough to excite them, and therefore for the time being they fall out of our purview. Molecules, however, do possess excited states, into which they may be transferred from the normal state by offering them one or two or three, or even a fraction of one equivalent volt of energy; and these they possess, even when jammed together in the liquid state.

These excited states of molecules correspond, according to modern theory, to various amplitudes of vibration of the atom-nuclei relatively to one another within the molecule. The simplest case, of course, is that of the diatomic molecule, of which there are so many examples—oxygen and hydrogen and nitrogen, for instance. The nuclei of the two atoms, being positively charged, repel each other; but the electrons, aided possibly by additional magnetic fields, exert upon each nucleus a force which tends to push them together; and there is a certain internuclear distance of equilibrium, for which the two opposing forces balance. If the nuclei are displaced slightly from their points of equilibrium, they vibrate. Vibration is a quantized form of motion; only certain amplitudes and certain energy-values are permitted. The low-energy excited states of the molecules correspond to the permitted amplitudes and the permitted vibration-energies; when a quantum excites one of these and rebounds with the remainder of its energy, the energy which it gives up is spent in augmenting the vibrations of the nuclei.

These low-energy excited states are responsible for Raman's discovery; partly because, as I have stated, they survive when the molecules are jammed together into a liquid—a fact which evidently means that the electrons, which produce the force upon the nuclei

countervailing their reciprocal repulsion, are shielded from the outer world, presumably by other electrons lying still farther outward from the nuclei; and partly because their energy-values are so conveniently low. This latter point can best be illustrated with an example. To perceive a relatively feeble optical effect, or one which is expected to be feeble, it is best to produce it in the visible spectrum—not merely in order to observe it with the eye; the major reasons are rather, that in

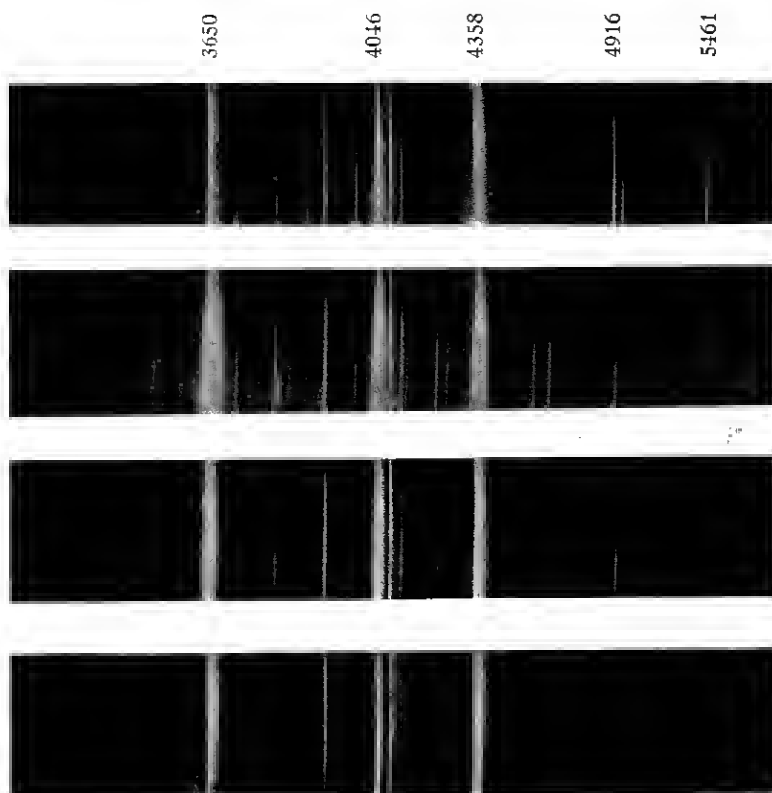


Fig. 2—At top, spectrum of primary light (mercury arc); below, spectra of light scattered by benzene, toluene, pentane respectively. (C. V. Raman; *Indian Journal of Physics*.)

going away from the visible spectrum-range in one direction we find the photographic plates becoming rapidly less sensitive, while in the other direction the transmission of the rays through matter grows steadily worse. Suppose then that one tries to produce the Raman effect by light near the high-frequency limit of the visible—say about 4000 \AA ., where the quantum-energy is about 3 equivalent volts. If

the scattered quantum in its turn is to be in the visible spectrum, its wave-length must be less than some 8000 Å., its energy more than roughly 1.5 equivalent volts. The primary corpuscle of light must therefore not cede to the molecule or atom more than $(3-1.5)$ or 1.5 equivalent volts of energy—the material particle must therefore be able to receive energy in quantities less than this, quantities preferably which are small fractions of an equivalent volt; its excited states should differ from the normal state by energy-differences of this order; and molecules satisfy this condition.¹²

En somme, then, the scattering of light with change of frequency was never discovered in all the abundant work on the common monatomic

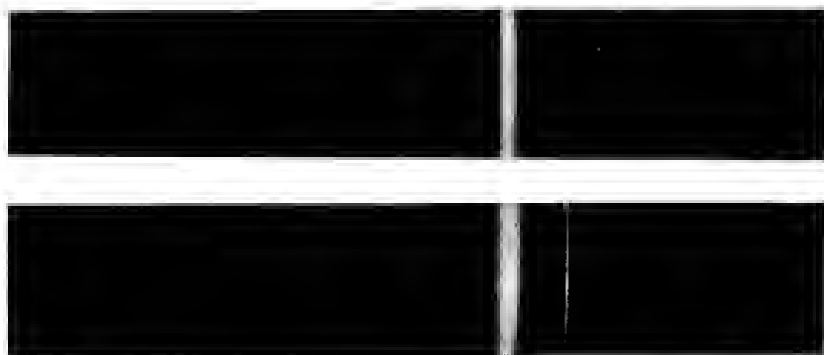


Fig. 3—At top, spectrum of primary light, reduced by a filter almost to a single strong line; below, that of light scattered by benzene, showing shifted lines due to that single line (4358). (C. V. Raman; *Indian Journal of Physics*.)

gases, because: first, the atoms were too few in unit volume to cause much scattering; second, they could not be squeezed together without destroying their power of entering distinct excited states; third, the excited states had energy-values so high, that a quantum of the visible or the near ultra-violet spectrum striking a normal atom would simply not have had energy enough to transfer it into one of them. It was discovered by Raman in the way in which he discovered it, because he was working with molecular liquids where: first, the molecules were numerous in unit volume and scattering was frequent; second, in spite of being squeezed together the molecules retained their power of enter-

¹² Atoms however do not always satisfy it; in particular, those of the noble gases and of mercury, the substances most often used in optical experiments on monatomic gases, possess no excited states differing from the normal state by less than four equivalent volts—another reason why the Raman effect was not sooner discovered. The more massive of the alkali metals have excited states superior to the normal by about 1.5 equivalent volts, while metals of the third column of the periodic table would be very favorable.

ing distinct excited states; third, the excited states had energy-values so low that a quantum of the violet, blue or green regions of the spectrum striking a molecule had plenty of energy to excite it and yet have some left over. Subsequently one of Raman's associates (Ramdas), photographing with very long exposure, detected the effect with ether vapor. Carrelli and his colleagues obtained it with molecular salts in aqueous solution;¹³ and perhaps in the course of time somebody may overcome the obstacles, and demonstrate the scattering of light with change of frequency by free atoms of a monatomic gas.

We will now consider some of the photographs which were made by Raman, and later with improvements of technique by Wood, Langer and Meggers, Brickwedde and Peters.

Some of Raman's earliest published pictures are reproduced in Fig. 2. At the top we see the spectrum of the primary light—that of the mercury arc, the source of light employed, I think, in all the researches thus far published. The strong lines near 4046 and 4358 are responsible for most of the Raman lines thus far observed by anyone; other strong lines are those near 5461, and the pair at 5770 and 5790. (These last look much fainter in Fig. 2 than in some of the others, but such variations are due to the photographic plates employed, and should not be heeded.) The three spectra below are, in order, those of the light scattered by benzene, toluene and pentane. The new lines are extremely numerous—so much so, that some care is required to determine for each new line which is the primary line whence it is shifted. This may be done by filtering out from the primary light all but one of its strong lines. In making the photographs in Fig. 3, Raman and Krishnan used a filter which removed from the infalling light almost all the quanta but those of the wavelength 4358 (though 3650 and 4046 are still seen dimly in the spectrum, the topmost one in the figure). The spectrum of the scattered light, below, now shows additional lines which are certainly made of quanta which originally had the wave-length 4358.

Figs. 4 and 5 show the spectra scattered by benzene and carbon tetrachloride, as photographed by Wood.¹⁴ The "fat" lines from left to right are the unshifted lines 4046, 4358, 5461 and the aforesaid doublet 5770–5790. (The rich adjacent spectrum is a "comparison" spectrum of iron.) Most of the lines companioning 4358 and 5461 on both sides are shifted lines. Notice, in the spectrum scattered by

¹³ With salts which are completely dissociated in solution they failed, as they expected, to obtain it. Possibly the effect may some day be used as a measure of percentage of dissociation!

¹⁴ I am much indebted to Professor Wood for furnishing me with prints of these, and to Dr. Langer for plates from which the next two figures were made.



Fig. 4—Light scattered by benzene (with comparison spectrum). The four fat lines from left to right are 4046, 4358, 5461 and the doublet 5770-5790 of the unshifted scattered light. (R. W. Wood.)



Fig. 5—Light scattered by carbon tetrachloride: note the array of lines shifted each way from 4358. (R. W. Wood.)

carbon tetrachloride, the triad of lines to the right of 4358, and the equally-spaced triad to its left. These latter are "anti-Stokesian" lines—I will presently explain the name—and consist of quanta which have received as much energy from molecules as the quanta of lowered frequencies have given up. With carbon tetrachloride they are extraordinarily bright. Notice again how these lines and the hazy doublet still further out are repeated to the right of 4046, where they are interspersed with other lines which are primary lines unshifted; and again on both sides of 5461.



Fig. 6—Ultraviolet light scattered by sulphuric acid; at the right, 2536 accompanied by numerous shifted lines. (R. M. Langer.)

In Fig. 6 we pass to another region of the spectrum, the ultra-violet. On the extreme right is the strong line 2536 of the mercury spectrum, scattered unshifted by sulphuric acid; the numerous lines beside it are Raman lines.

In Fig. 7 the scattering substance is water; the novel feature of the scattered light is a set of diffuse bands, each shifted from a certain line of the primary spectrum. It is frequently observed that the shifted lines, and the unshifted lines as well, are broader and hazier than those of the primary light, an effect attributed to conversion of the energy of the quanta into energy of rotation of the molecules. Water however shows a quite remarkable broadening, if this be the



Fig. 7—Light scattered by water; note the diffuse bands shifted from the sharp lines. (R. M. Langer.)

way to describe it; it has been attributed to association of molecules.

A few special words must be said about the shifted lines which are of higher frequency than the primary light responsible for them—not because they are really more remarkable than the others, but because somehow they seem less to be expected. They are called by the monstrous name "anti-Stokesian" because in fluorescence such lines run counter to a principle laid down by Stokes; it seems cruel to perpetuate a mistake in this way. They consist of quanta which have

received energy from the molecules which they have struck. They must therefore have struck molecules which were not originally in the state of lowest energy, or "lowest state" for short. Such a molecule might have been in the lowest state, until some antecedent quantum came along and gave it energy, lifting it into a higher state; the second quantum then undid the work of the first, taking away the energy which the first had given and being shifted as far towards higher as the former towards lower frequencies. It does not seem likely that this double process occurs often, although pairs of lines with equal and opposite shifts are reported in several cases. Much more commonly, in all probability, the molecules which at any moment are in other states than the lowest are there because of the interchanges of energy which are always taking place between the particles of substances in thermal equilibrium. The laws of thermal equilibrium are such, that if in a substance at room-temperature the molecules have one or more excited states differing from the lowest state only by fractions of a volt, quite an appreciable fraction among them are at any moment in one or another of those states. The higher the temperature, the greater this fraction; in consonance with which fact it is observed, that the warmer the scattering liquid the more prominent are these "anti-Stokesian" lines.

The shifted lines, in the light scattered at right angles to the primary beam (the only direction which has been utilized to any extent), are partially polarized. The electric vector is stronger in the direction perpendicular to the primary beam than in the direction parallel to it, as one would expect. The degree of polarization varies enormously from one shifted line to another, and may be either greater or less than that of the unshifted lines. Cabannes thought it to be constant for lines shifted by the same amount from different primary lines, but the ampler data of Carrelli do not seem to bear him out.

The test for "coherence" of the shifted light, which is made by bringing the scattering substance near to the state of "critical opalescence" where the irregularity of the arrangement of the atoms is greatest—the shifted lines should brighten *pari passu* with the unshifted, if their light is coherent—has been made by at least four people (Raman, Bogros and Rocard, Martin); but the results are oddly discordant.

One more most valuable service of the shifted lines remains to be mentioned. In the foregoing pages I have stressed the fact that some of them are known to agree, that is to say their frequency shifts are known to coincide, with the frequencies of lines of the infra-red spectrum of the scattering substance. But there are cases in which the

infra-red spectrum of the scatterer has not yet been explored; and there we may deduce its lines from the frequency-shifts of the Raman lines in the visible spectrum. Moreover, there are regions of the infra-red spectrum which are very difficult to explore, because of such technical reasons as the insensitiveness of photographic plates; and the Raman lines make it possible to discover some at least of the features of these, by observations made in the most convenient region of the spectrum. Perhaps this will turn out to be the most fruitful of the consequences of Raman's discovery.

SCATTERING OF LIGHT WITH TRANSFER OF ENERGY TO VIBRATIONS IN SOLIDS

The scattering of light with shift of frequency from solids was discovered, independently and almost simultaneously, by C. V. Raman and K. S. Krishnan in India and by G. Landsberg and L. Mandelstam in Russia. As seen on the photographs of the spectra of the scattered light, the effect is altogether like the Raman effect of liquids and vapors. The lines of the primary spectrum, scattered without change of frequency, are accompanied by companions shifted mostly towards lower, but in occasional cases towards higher frequencies. The infalling quanta therefore sometimes cede energy to quantized motions within the solid substance, and sometimes—but much less frequently—receive energy from these.

The first and obvious question is: do the frequency-shifts agree with lines of the infra-red spectra of the solid substance? For studying the infra-red spectra of solids there are, be it remembered, two classical methods. One is the familiar way of dispersing a beam of light which has traversed the solid, and looking for absorption lines or bands in its spectrum. To find a good dispersing-agent in the far infra-red is however not easy; and there is an alternative method, in which the beam of light is reflected several times over from samples of the solid. At each incidence of the beam upon the crystal, the waves of frequencies which do not coincide with natural frequencies of the substance go on through, while the waves of frequencies which do coincide are mostly reflected. Thus, after several reflections, the "residual" beam is composed of one or a few wave-lengths, those of the principal absorption-lines of the crystal; and these are measured by operating on the beam with a special interferometer, or in some other way. This is the method of "residual rays," or "Reststrahlen," which was developed and much exploited during the nineties of the last century and the opening years of this. The spectrum-lines of the crystalline substance are its "Reststrahlen"; and these are to be compared with the fre-

quency shifts observed in and near the visible spectrum. Here is an instance: Landsberg and Mandelstam working with quartz observed frequency-shifts corresponding to infra-red lines of wave-lengths 9μ , 13.5μ , 21.5μ , 48μ , and 81μ respectively; there are Reststrahlen of wave-lengths 8.7, 12.8 and 20.7 , while the other two wave-lengths cited lie in gaps of the infra-red spectrum unexplored as yet.

A photograph by F. G. Brickwedde¹⁵ which I reproduce as Figure 8 illustrates this effect. The very broad black band is due to primary light of wave-length about 2536, scattered without change of fre-

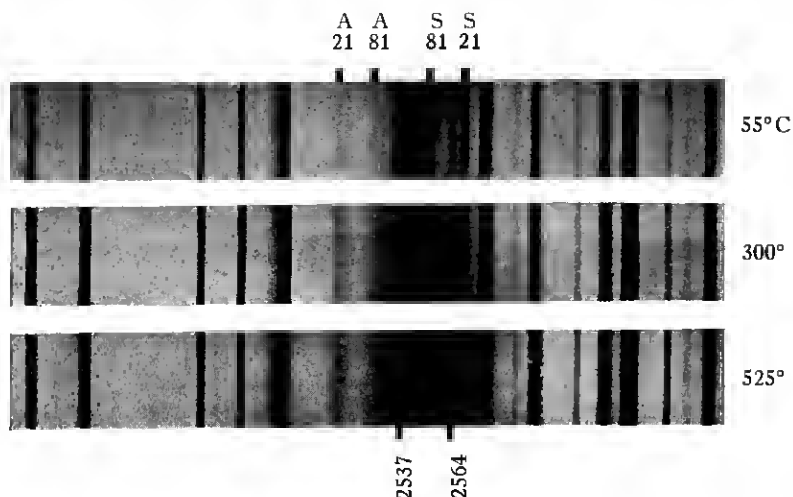


Fig. 8—Light scattered by a quartz crystal; unshifted line is 2536, lines denoted by S and A are shifted towards lower and higher frequencies respectively. (F. G. Brickwedde.)

quency; its excessive width is due to the great intensity of this light. The lines marked S21 and S81 consist of quanta which have spent part of their energy in exciting vibrations, those corresponding to the Reststrahlen of wave-lengths 21μ and 81μ respectively. The lines marked A21 and A81 consist of quanta which have received energy from these vibrations. These "Anti-Stokesian" lines evidently grow more intense as the temperature of the crystal is raised, as they should, for the reason which I have already stated: as the substance grows warmer, the percentage of the molecules spontaneously in vibration is increased. In addition, the shifted lines all move inward toward the position of the unshifted light as the temperature rises—one may see this by comparing those on the low-frequency side with

¹⁵ I am much obliged to Dr. Brickwedde for furnishing me with a print of this photograph.

the line marked 2564, which is a faint line of the primary light scattered without change in frequency. This diminution in the shift signifies that the natural frequencies of the lattice-vibrations are declining, which is to be expected from the expansion and relaxation of the crystal which the rise of temperature brings about.

There arises now an interesting question. X-ray analysis reveals that there are certain chemical compounds, organic chiefly, of which the molecules retain their identity when crystallization occurs; they set themselves side by side in a regular lattice, but the arrangement of the atoms in each of them is not greatly altered. At the other extreme, there are compounds of which the molecules disintegrate completely when solidification takes place, and the atoms arrange themselves without any reminiscence of their earlier relations; a familiar instance is sodium chloride, in the crystal of which every atom of either kind, Na or Cl, is surrounded by six of the other kind all equally distant from it. Intermediate cases occur, as for instance that of CaCO_3 , where each atom-group or "radical" CO_3 retains its identity but not its coupling to one single Ca atom. Now when molecules or radicals survive within the crystal, oscillations of atoms inside these atom-groups are probably not different in character from the oscillations which occur within the same molecules when they are wandering freely in a liquid or a gas. But in the case of a crystal like sodium chloride, the oscillations must be controlled by the forces which hold the atoms of the crystal together; they are truly lattice-vibrations. Perhaps the difference between the two is not really profound; but it will be interesting to find out whether quanta may or may not transfer energy with equal ease to vibrations of either type, *i.e.* whether in the two cases the shifted lines are comparably bright. According to Carrelli, Pringsheim and Rosen, all of the shifted lines thus far observed with solids, except probably those obtained with quartz, correspond to vibrations within molecules or radicals which remain intact in the crystal.

THE COMPTON EFFECT

The Compton effect, in the restricted sense—the sense in which I shall use the term—is simply the scattering ensuing on collisions of corpuscles of light with free electrons. So much has been written about the effect¹⁶ that it is scarcely necessary for me to do more in this place than mention the laws of these collisions. The energy which the quantum loses is converted into kinetic energy of translatory

¹⁶ Cf. for instance this *Journal*, April, 1925; "Introduction to Contemporary Physics," pp. 146–160; H. Kallmann, H. Mark, "Ergebnisse der exakten Naturwissenschaften," 5 (1926).

motion of the electron. Momentum also is conserved in the encounter; the momentum of the quantum is equal in magnitude to hn/c before and to hn'/c after the collision, n and n' standing for the frequency before and after; these momenta are of course vectors parallel to the directions along which the corpuscle of light approaches and recedes, respectively; and their difference is the momentum which the electron acquires. These two conditions limit very severely the transfer of energy from quantum to electron. All of the quanta deflected through a given angle from their original line of flight suffer the same loss of energy and the same shift in frequency. The relation between shift of frequency and angle of deflection θ takes its simplest form when we write it as a relation between shift of wave-length, $\Delta\lambda$, and angle θ :

$$\Delta\lambda = \frac{h}{mc} (1 - \cos \theta).$$

The maximum shift of wave-length occurs when the quantum is reflected straight backward along its original line of approach; it is evidently $2h/mc$, and the corresponding maximum frequency shift is $2hn^2/mc^2$, as I stated earlier.

The predicted relation of wave-length shift and angle of scattering has been verified to the most thoroughgoing extent;¹⁷ and the recoiling electrons have been observed as they dash off with the energy which the corpuscle of light has lost. Research on the Compton effect is now confined almost entirely to the problem of its likelihood of occurrence—*i.e.*, given a substance with P atoms per unit volume irradiated by a stream of X-rays composed of N quanta per unit area per second, what are the relations between the number of these quanta which are scattered in the fashion just described, and the frequency of the X-rays and the nature of the atoms? The corresponding problem for the Raman effect will undoubtedly soon come into the foreground. It is, of course, slightly annoying that we do not know *a priori* how many of the electrons of (say) the carbon atom, or how many of the electrons in a piece of graphite, are to be regarded as “free” electrons. This seems to be one of the facts which we shall have to deduce as best we may from these researches on the likelihood of the Compton effect. The data thus far acquired may be summarized in this way: the higher the frequency of the quanta, and the lower the mass of the atoms, the more abundant these collisions are. High-frequency X-rays poured

¹⁷ Even to the point where with general assent it is taken for granted and the measurements are used as data for evaluating the constant m , the mass of the electron!

upon lithium or paraffin give the best "yield"; visible light, none perceptible.

The shifted X-rays scattered at 90° are polarized, very nearly completely (Lukirsky, Kallmann and Mark).

THE SCATTERING OF QUANTA ATTENDED BY EXTRACTION OF BOUND ELECTRONS

Almost immediately after Arthur Compton had measured and interpreted the scattering which is due to collisions of quanta with free electrons, he and others realized that corpuscles of light might possibly encounter atoms in such a way that they extracted bound electrons, and thereupon were scattered with a corresponding abatement of their energy. In fact it seemed most probable that the electrons responsible for the Compton effect were themselves not quite free, but very lightly bound; and that a careful study of the scattered quanta, the "shifted" or "modified" line, would reveal that they had spent energy in dissolving the bonds as well as in imparting kinetic energy to the electrons. Researches on this topic were numerous, and are still continuing. At that time, the Raman effect had not yet been discovered; and perhaps it did not seem natural to accept the transfer of energy from corpuscles of light to atoms as a *general* phenomenon, apart from special cases so easy and so beautiful to visualize as the elastic impacts of quanta against free electrons. At all events, when in 1923 and 1924 data were published by G. L. Clark and W. Duane which to the present-day onlooker seem to declare the effect in the most forthright fashion, they made no such impression.

The experiments of Clark and Duane were involved in a long controversy, in which the reality even of the Compton effect was called into question. Data were obtained by some experimenters, which others could not or at least did not reproduce. The questions at issue speedily reached the point, where no outsider could risk a judgment unless he was himself a great expert in the study of X-ray scattering. Unfortunately the experiments were terminated, when the reality of the Compton effect was established. I say "unfortunately," for it now seems as if in the nature of things both sides must have been right. Compton had discovered the transfer of energy from quanta to free or nearly free electrons; Clark and Duane must have discovered the transfer of energy from quanta to bound electrons, or the process in which a corpuscle of light uses part of its energy in ionizing an atom, part in giving speed to the liberated electron, and retains the remainder. It would be a very desirable result of the present-day revival of interest in scattering, if somebody should reinvestigate this entire field.

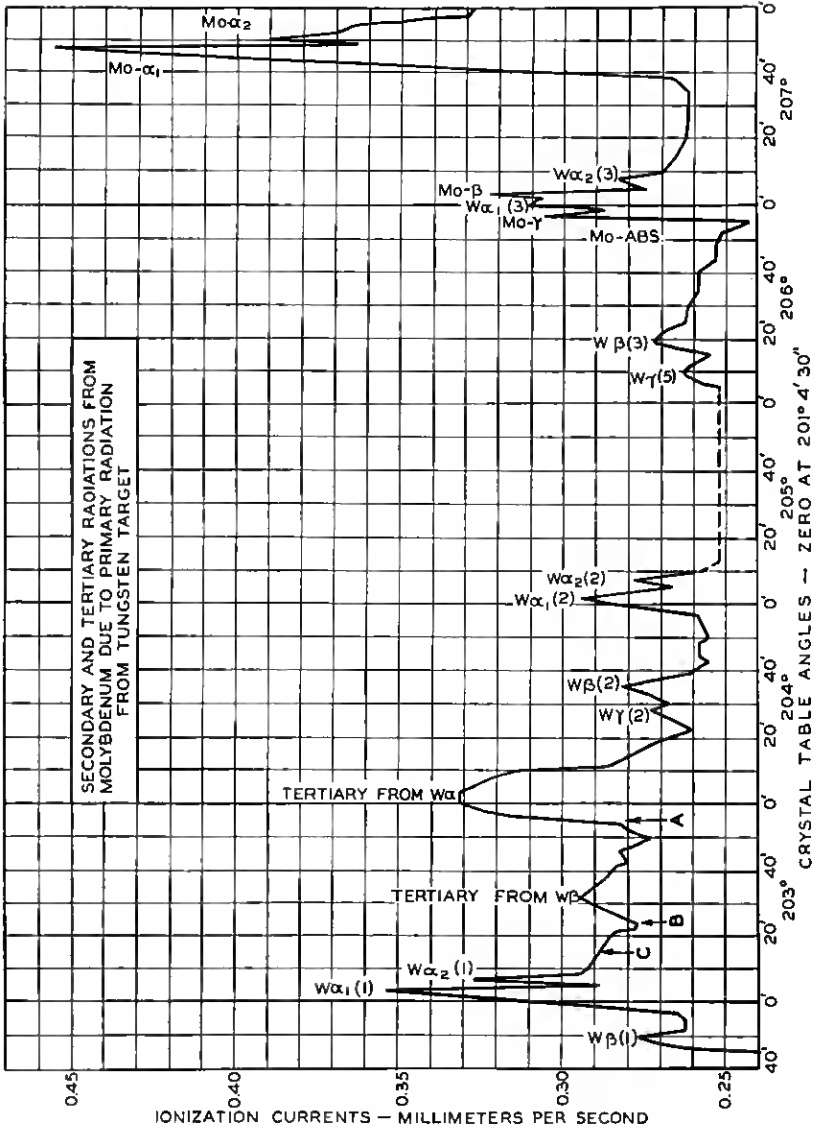


Fig. 9—X-rays scattered by molybdenum, the sharply-pointed peaks being unshifted lines. (G. L. Clark, W. Duane; *Proc. Nat. Acad. Sciences.*)

I will pass over the theory first propounded for these data, which I have quoted elsewhere, and over the paper in which Compton advanced practically the present theory; and reproduce one of the spectrum-curves of scattered radiation from the work of Duane and Clark. This curve represents the scattering of high-frequency X-rays by molybdenum. The primary light was composed of several lines, the various lines of the *K*-spectrum of tungsten. In the scattered spectrum, these lines appear unshifted as narrow sharp peaks. We consider the two at the extreme left, and then the two humps which rise from the points marked *B* and *A*. These points correspond to the wave-lengths of quanta which originally belonged to the spectrum-lines at the extreme left, and have lost exactly the energy necessary to extract a *K*-electron from the molybdenum atom. The humps in all probability are composed of quanta, which have extracted such electrons and in addition have given them greater or smaller amounts of extra kinetic energy.

Years after the work of Clark and Duane had been discontinued, Bergen Davis and D. P. Mitchell undertook to study what they designated as the "fine structure" of the lines in the spectra of scattered X-rays. They had many improvements of technique at their disposition, improvements many of which were due to Davis himself; for instance they had a spectrometer of Davis' design, by which it was possible to appreciate the true narrowness of a very narrow X-ray line, instead of having it spread out by defects of the apparatus into a simulation of a wide band. They irradiated graphite with the spectrum-line known as $K\alpha_1$ of molybdenum, of which the wave-length is 0.721 \AA. ; and in the spectrum of the rays scattered at 90° they found not only this line, but four others of slightly greater wave-lengths of which three are shown in Fig. 10. The outermost, beyond the right-hand limit of the picture, comprises quanta which collided with free electrons—it is the Compton shifted line. The outermost of the other three consists of incident quanta which have given up just the amount of energy required to extract one of the *K* electrons—one of the pair which are by far the most tightly bound of all the six which belong to the carbon atom. More precisely, the extraction energy of these electrons is evaluated from the X-ray spectrum of carbon at 287 equivalent volts, while the loss of energy suffered by the quanta is estimated by Davis and Mitchell at 279; the difference of less than 4 per cent is within the uncertainty of experiment. The two innermost of the shifted lines, composed as they are of quanta which have yielded up 29 and 50 equivalent volts respectively, are presumably tokens of collisions in which superficial electrons were torn away from carbon

atoms. That their shifts do not agree very well with the values of extraction-energies suggested by certain spectroscopic data is not in the least surprising. None of the spectroscopic data was obtained with solid carbon; and the superficial electrons of the atom are most sensitive of all to such changes of environment as occur when it is incorporated into a lattice. In all probability, the frequency-shifts of these lines, when divided by h , are the best values yet available for the amounts of energy required to extract superficial electrons from carbon atoms in the graphite lattice.¹⁸

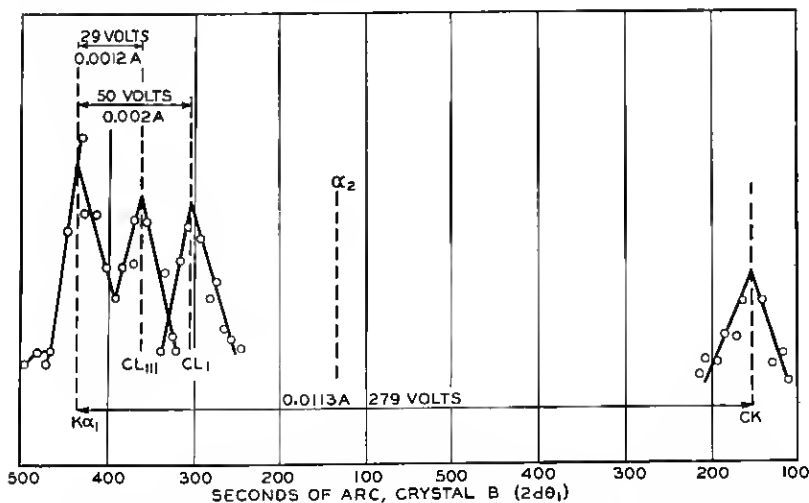


Fig. 10—X-rays scattered by graphite, the peak on the left being the unshifted line. (B. Davis, D. P. Mitchell; *Physical Review*.)

Davis and Mitchell point out a feature of these scattered rays which should be stressed: the shifted lines are sharp, implying that the quanta simply extract electrons, without endowing them with divers quantities of kinetic energy to boot. They later observed such lines in the rays scattered by aluminium.

THE GENERAL PRINCIPLE

The general principle of which all these scattered phenomena of scattering are special illustrations now stands forth very clearly, and

¹⁸ It seems paradoxical that the quanta which collide with free electrons should confer on them several hundred of equivalent volts of energy, while those which strike these loosely-bound superficial electrons should lose but half-a-dozen. The contrast is due to the requirement of conservation of momentum; where only two particles are involved the relatively large energy-transfer is entailed, but where there are three among which the momentum may be divided, the limitation ceases.

may be expressed in any of several ways, laying greater emphasis now on one aspect and now on another.

From the viewpoint of the atom, and using the notions of the undulatory theory, one may say that *the atom (or the molecule) modulates the incident light with frequencies of its own.*

Again from the viewpoint of the atom, but using now the notions of the corpuscle-theory of light, one may say that *the atom or molecule may take part but not necessarily all of the energy of an incident quantum, converting this energy in any of numerous ways.*

From the viewpoint of the quantum, however, the essential feature of the principle is this: *a quantum may lose part of its energy or receive energy in an encounter with a molecule or atom, retaining its identity even though its frequency is changed.*

The first who stated the principle with anything like its proper generality was probably Smekal; in the following year (1924) it was developed by Kramers and Heisenberg. They knew of no examples but the Compton effect, and curiously enough no one was tempted to search for other instances, though Foote and Ruark considered whether any of the phenomena already known in optical spectra could be related to it.¹⁹ Partial anticipations crop out here and there, especially in the work of Compton, Jauncey and their associates; for it was early suspected that the electrons responsible for the Compton shift are not altogether free, but very loosely bound to atoms; it was assumed that the incident quanta must spend energy enough to break the bonds as well to set the electrons into motion, and efforts were made to disclose this breaking of the bonds.²⁰

It is the third of the foregoing formulations of the principle which I wish to stress in closing—the principle from the viewpoint of the quantum, the authorization of the quantum to give up part of its energy and retain the rest. To the unprejudiced mind this must seem very natural. We have accepted for years the principle that an electron may give up part of its energy and keep the rest—that the life-history of an electron is an endless sequence of gains and losses of kinetic energy, of speedings-up and slowings-down, during which the identity of the electron is never lost. Why should we not have thought likewise about the quantum? Yet it has been almost an article

¹⁹ I am told that Kramers tried vainly to persuade a number of experimental physicists to look for the effect. At present they must be feeling like the astronomers whom Adams vainly pressed to make haste in looking for the planet Neptune, until finally someone else discovered it.

²⁰ Jauncey and Compton anticipated in 1927 the idea that atoms in a lattice may acquire energy of vibration from incident quanta, and discovered an important restriction which should be noted; apparently the lattice or some third particle must be involved in the impact.

of faith that a quantum must give all of its energy, or none—either vanish altogether, or retain its frequency unchanged.

Of course, till 1922 there was no compelling evidence that a corpuscle of light may suffer a change of frequency in rebounding from a particle of electricity or matter. However, it does not seem to have occurred to anyone that the want of evidence was in any way surprising, or that it should be possible to find quanta scattered with change of energy. The reason for this satisfaction, I suspect, was perfectly simple. It did not seem possible that a quantum should give up part of its energy, for its energy was inseparably linked with its frequency, and its frequency seemed to be its one indissoluble and characteristic feature. As well say that an electron might lose part of its charge and still be the same electron, or that an atom might lose part of its mass and yet remain the same atom, as that a quantum might give up part of its frequency without ceasing to be itself!

Now this contention—if one may call it a contention—lost its force through the discovery that electrons also are endowed with frequency and wave-length, or in other words that negative electricity like light possesses both qualities of corpuscles and qualities of waves. Whenever a corpuscle of electricity parts with kinetic energy, whenever a corpuscle of light parts with energy, the associated wave-length is augmented. If we suppose that an electron retains its identity when its wave-length changes, how can we deny like continuity of existence to a quantum? If we admit that an electron may suffer change of wave-length in rebounding from an atom, how may we be surprised when a quantum does the like? It is true that the corpuscle of electricity has other features than wave-length: a charge which apparently never changes, a mass which apparently never falls below a certain minimum. The quantum does not have an immutable quality corresponding to charge, and we do not know of any lower limit to its mass short of complete disappearance. But for either sort of corpuscle the wave-length is in principle variable. We say that all electrons are of one kind, but may have any speed. Should we not also say that all quanta are of a single kind, though they may have any frequency?

BIBLIOGRAPHY

(The year is 1928, unless otherwise stated)

- S. K. ALLISON, W. DUANE: *Proc. Nat. Acad. Sci.*, *10*, pp. 196–199 (1924).
 J. A. BECKER: *Proc. Nat. Acad. Sci.*, *10*, pp. 342–345 (1924).
 C. E. BLEECKER: *Zs. f. Phys.*, *50*, pp. 781–786.
 A. BOGROS, Y. ROCARD: *C. R.*, *186*, pp. 1712–1713.
 M. BORN: *Naturwiss.*, *16*, p. 673.
 F. G. BRICKWEDDE, M. F. PETERS: *Bull. Amer. Phys. Soc.*, Nov. 15.
 M. DE BROGLIE: *C. R.*, *187*, p. 697.
 J. CABANNES: *C. R.*, *186*, pp. 1201–1202, 1714–1715; *187*, pp. 654–656.

- J. CABANNES, P. DAURE: *C. R.*, *186*, pp. 1533-1534.
 A. CARRELLI, P. PRINGSHEIM, B. ROSEN: *Zs. f. Phys.*, *51*, pp. 511-519.
 G. L. CLARK, W. DUANE: *Proc. Nat. Acad. Sci.*, *9*, pp. 413-424 (1923); *10*, pp. 41-47, 92-96, 148-152, 191-196 (1924).
 A. H. COMPTON: *Phys. Rev.*, (2) *24*, pp. 168-177 (1924).
 A. COTTON: *C. R.*, *186*, pp. 1475-1476.
 B. DAVIS, D. P. MITCHELL: *Phys. Rev.*, (2) *31*, p. 1119; *32*, pp. 331-335; *Bull. Am. Phys. Soc.*, Dec. 12.
 P. DAURE: *C. R.*, *186*, pp. 1833-1835; *187*, pp. 940-941.
 K. K. DARROW: *Science*, *68*, pp. 488-490.
 P. D. FOOTE, A. E. RUARK: *Science*, *61*, pp. 263-264 (1925).
 R. V. L. HARTLEY: *Bull. Am. Phys. Soc.*, Dec. 12.
 G. E. M. JAUNCEY, A. H. COMPTON: *Nature*, *120*, p. 549 (1927).
 H. KALLMANN, H. MARK: *Zs. f. Phys.*, *36*, pp. 120-142 (1926).
 E. H. KENNARD: *Bull. Amer. Phys. Soc.*, Dec. 12.
 H. KORNFIELD: *Naturwiss.*, *16*, p. 653.
 H. A. KRAMERS, W. HEISENBERG: *Zs. f. Phys.*, *31*, pp. 681-706 (1925).
 H. S. KRISHNAN: *Nature*, *122*, pp. 477-478, p. 650.
 G. LANDSBERG, L. MANDELSTAM: *Naturwiss.*, *16*, pp. 557-558; *C. R.*, *187*, pp. 109-111.
 R. M. LANGER, W. F. MEGGERS: *Bull. Amer. Phys. Soc.*, Nov. 15.
 F. A. LINDEMANN, T. C. KEELEY, N. R. HALL: *Nature*, *122*, p. 921.
 P. LUKIRSKY: *Nature*, *122*, pp. 275-276.
 W. H. MARTIN: *Nature*, *122*, pp. 506-507.
 P. PRINGSHEIM: *Naturwiss.*, *16*, pp. 597-605; *Zs. f. Phys.*, *50*, pp. 741-755.
 I. RAMAKRISHNA RAO: *Indian Jour. of Phys.*, *3*, pp. 123-130.
 C. V. RAMAN: *Indian Jour. of Phys.*, *2*, pp. 387-398.
 C. V. RAMAN, K. S. KRISHNAN: *Nature*, *121*, pp. 501-502, 619, 711; *122*, pp. 12-13, 169, 278; *Indian Jour. of Phys.*, *2*, pp. 398-420.
 L. A. RAMDAS: *Nature*, *122*, p. 57; *Indian Jour. of Phys.*, *3*, pp. 131-136.
 Y. ROCARD: *C. R.*, *186*, pp. 1107-1109; *Annales de Physique*, *10*, pp. 116-232.
 A. E. RUARK: *Nature*, *122*, pp. 312-313.
 M. N. SAHA, D. S. KOTHARI, G. R. TOSHNIWAI: *Nature*, *122*, p. 398.
 A. SMEKAL: *Naturwiss.*, *11*, pp. 873-875 (1923); *16*, pp. 612-613 (1928).
 S. VENKATESWARAN: *Indian Jour. of Phys.*, *3*, pp. 105-122.
 D. L. WEBSTER: *Proc. Nat. Acad. Sci.*, *10*, pp. 191-196 (1924).
 R. W. WOOD: *Nature*, *122*, p. 349; *Phil. Mag.*, (7) *6*, pp. 729-742.